Journal of Ceramic Processing Research. Vol. 3, No. 2, pp. 66~69 (2002)

J O U R N A L O F
Ceramic Processing Research

Laser beam sintering of thin alumina coatings on metals

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This paper is focussed on introducing technology and results of a laser sintering process. Laser beam sintering of alumina coatings on metals was investigated as a part of a joint project carried out by the Fraunhofer IKTS Dresden and the Laserinstitut Mittelsachsen e.V. (Laser Institute of Middle Saxony, LIM). The IKTS team developed a method for deposing alumina powder on a metal surface by electrophoretic deposition. The powder layer was characterised by a grain size of about 200 nm and a high density. These properties enable a sintering temperature below the metal's melting point. The LIM group developed a technology for sintering the powder layer by laser beam. The results achieved were very promising. The layer of a thickness of about 10 µm adhered well and had a low porosity and high hardness. Applications based on this technology are expected in several branches.

Key words: wear-resistance, protective ceramic coating, hardening.

Introduction

Often industry requires metal assemblies with particular high hardness or high temperature, chemical or wear resistance. Many investigations have been carried out to develop a suitable technology for coating metals with ceramics as a tribological and corrosional protection layer.

One preferred method is the plasma spraying of ceramics. The disadvantages of this method may result from a very rough and thick coating, relatively high porosity or large solidified grains in the coating [e.g. 1, 2, 3, 4, 5]. Sometimes a remelting process on the surface is necessary often and this is done by a laser beam [6, 7].

Another method is the direct melting of ceramic powder layers. In this case, cracks may often appear.

However, the hardness achievable by these technologies is limited.

Coatings generated by physical or chemical vapour deposition (PVD or CVD) processes are controllable and of good quality, but only up to a thickness of a few micrometers [8, 9]. These processes themselves are expensive and take a long time.

In conventional sintering processes in a furnace, it has been shown to be impossible to achieve crackfree layers [10].

To overcome this situation, the aim of the current research was to develop a technology enabling coatings of pure aluminium oxide with a small and controllable grain size, high density, high hardness and high adherence.

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Experimental set-up

Two kinds of steel substrates were used: type 1.4301 and 1.3981. The specimen size was 40×15 mm with a thickness of 2 mm. They were electrophoretically coated with alumina powder from a solution by the Fraunhofer IKTS Dresden. The layer thickness was 10-30 µm. The material compositions and some of their properties are shown in the following Table 1:

For the laser treatment, a shielding gas chamber was used due to the high reactivity of the steels. A photograph of the chamber is given in Fig. 1:

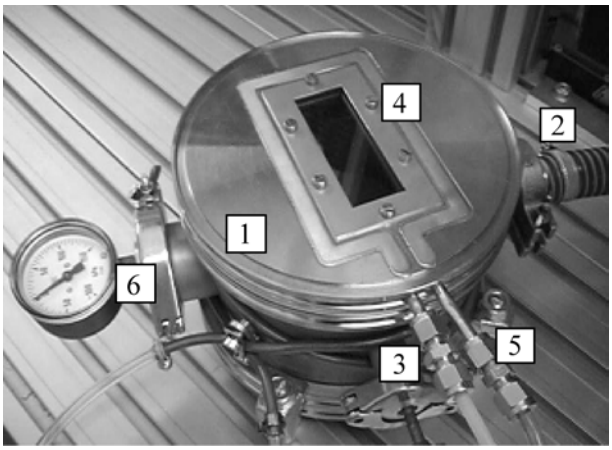
After evacuation, the chamber was refilled with He up to a pressure of about 50 mbar.

For the laser treatment, two different kinds of lasers were used.

1. A continuous wave (cw) CO_2- laser (wavelength of

Table 1. material compositions and properties

	Steel 1.4301	Steel 1.3981	Alumina
Chemical analysis	C: 0.07% Si: 1.0% Mn: 2.0% P: 0.045% S: 0.03% Cr: 19.0% Fe: Residue	Ni: 29% Co: 18% C: 0.03% Mn: 0.3% Si: 0.2% Fe: Residue	Al_2O_3 99.99%
Vickers Hardness	168	150	2000
Melt. Temp.	1,450°C	1,450°C	Sintering temperature: 1100°C
thermal expansion coefficient	11.7×10^{-6} K^{-1}	7.6×10^{-6} K^{-1}	7.5×10^{-6} K^{-1}



1: Shielding gas chamber 2: Connection to the vacuum pump
3: Connection to the shielding gas 4: Window for the laser beams
5: Cooling water inlet 6: Manometer

Fig. 1. Shielding gas chamber for the laser sintering process.

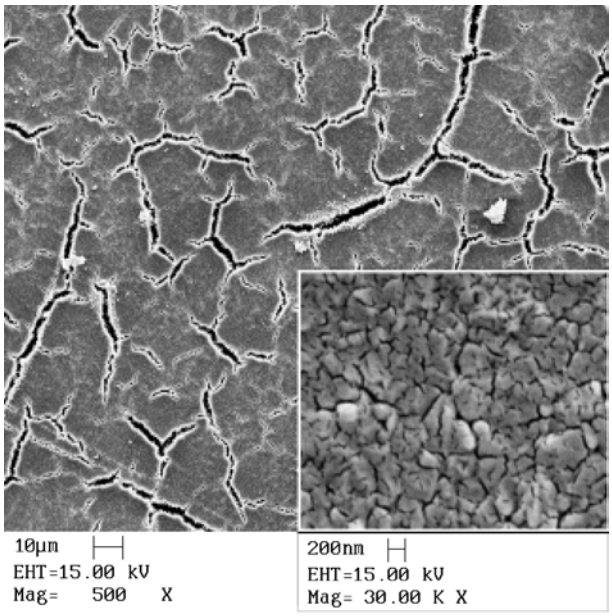


Fig. 2. SEM- view of the sintered coating surface. (Thickness of the coating not sintered: 12 µm, heating rate = 0.35 Ks^{-1}, ϑ_s = 1,400°C, t = 200 s, cooling rate = free, shielding gas)

10.6 µm) with a output power up to 600 W.

This beam was scanned across the surface of the coated metal, inducing an equal temperature field over the whole area.

2. A Nd: YAG- laser beam (wavelength of 1.06 µm) with a cw output power up to 1000 W. Its beam was transmitted through a fibre and extremely defocused on to the material surface. This laser was applied to guarantee a homogenous energy input.

The temperature was measured with a pyrometer and controlled by variation of the laser power. Adjustments made were mainly concentrated on heating velocity, sintering temperature and cooling velocity.

The surface, as well as cross sections, were investigated by scanning electron microscopy.

Micro-hardness measurements of the sintered coatings were carried out with a method of dynamic loading, at a load of 20 mN, a loading rate of 0.44 mN s^{-1} within a period of 30 s at the centre of polished cross sections. These measurements were done by the Fraunhofer IKTS Dresden.

Results

Sintering on steel 1.4301 by CO_2- laser beam

Sintering of the powder layer took place over a temperature range of 1,400-1,500°C (arrest time 200 s). The above temperatures are critical as the metallic substrate starts melting. Lower sintering temperatures are also possible, but they result in longer arrest times. A significant influence on grain size as a function of the operating temperature could not be found. The mean grain size of the sintered layer was about 300 nm. The heating rate is of special influence: Rates ($\Delta\vartheta\uparrow$) higher than 0.7 Ks^{-1} caused the coating to spall off instantly.

However, all sintered coatings showed cracks. They were spread across the surface in a pattern with a crevice width of about 3 µm. Only the centre of the coating between the cracks is well connected with the substrate.

An SEM micrograph of the sintered surface with a magnified area between the cracks is shown in Fig. 2.

Sintering on steel 1.4301 by Nd: YAG- laser beam

In the case of these investigations as well, it was impossible to achieve a surface free of cracks. The temperatures for the sintering process of the coating by use of the Nd:YAG laser are nearly the same as when using a CO_2- laser beam: 1,300-1,500°C.

Otherwise, the different wavelengths showed completely different results. Without an influence on the coating adherence the heating rate could be raised to 2 Ks^{-1}. A further increase was not possible due to technical limits. In other words the heating rate could be more than five times higher than for the CO_2- laser heating. In contrast to the heating rate, the cooling rate was critical. Thus, free cooling resulted in flaking off some coating clusters. Consequently, controlled cooling was necessary. Furthermore, extreme grain growth was obtained. In spite of the shorter heating time and after minimizing the arrest time, the minimum grain size achieved was 1 µm (a fivefold increase of the original).

Nevertheless, an interesting phenomenon could be observed: The cracks were annealed at temperatures at the beginning of forming a liquid phase of the metal. It could be shown that small amounts of the metal

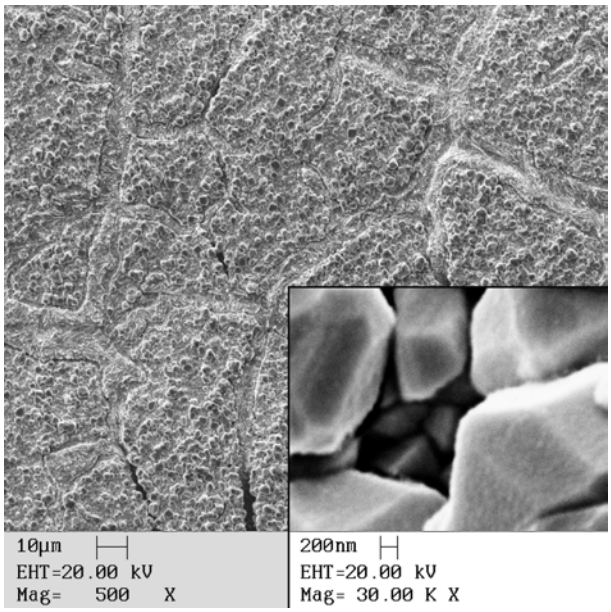


Fig. 3. SEM- view of the sintered coating surface with annealed cracks. (Thickness of the unsintered coating: 10 µm, heating rate = 2.0 Ks^{-1}, ϑ_s = 1,500°C, t = 100 s, cooling rate = 0.38 Ks^{-1}, shielding gas)

liquid filled the crevices up to the surface. On the surface, the metal is suffused by a 3 µm thick layer of a solid solution of Al, Fe and O. An example of this is shown in Fig. 3. The presence of a liquid phase during the sintering process may also be responsible for the intensive grain growth mentioned above.

It is difficult to reproduce the build up of sintered layers this way. It is necessary for only the surface of the metal to start melting. A voluminous melting leads to a wavy deformation of the surface.

To explain what happens, we have to distinguish two main processes:

1. Recapitulating, the shorter wavelength of the Nd:YAG- laser beam seams to be more suitable than the longer wavelength of the CO_2- laser beam. It is assumed that the absorption coefficient is responsible for the behaviour obtained.

In case of the CO_2- laser radiation, about 63% of the absorbed laser power will be absorbed in alumina at a depth of 1 µm. That means that sintering of the coating itself has already begun when the metal is heated up. This results in two contrary material movements: the ceramic is shrinking by sintering, whereas the metal expands. The temperature gradient between both materials is high. A large misfit in mechanical stresses occurs.

In case of the Nd:YAG- laser, the radiation is nearly completely transmitted through the alumina coating. The heating of the ceramic is forced by the increasing absorption coefficient of this material with temperature. Absorption on the underlying metal surface leads to indirect heating of the coating. Temperature differences

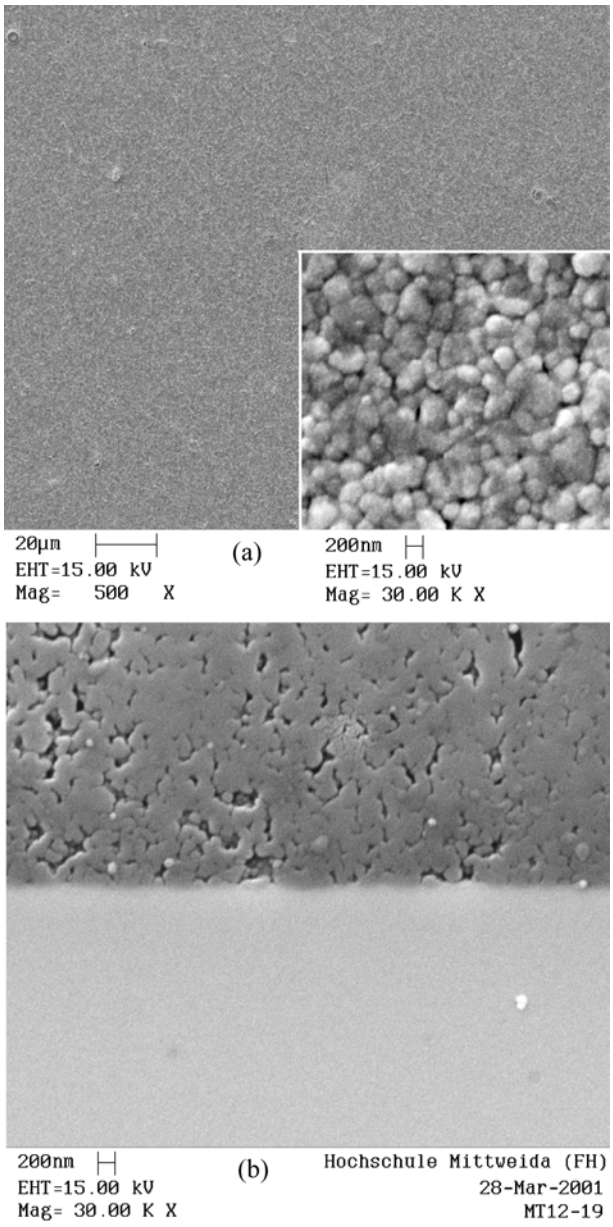


Fig. 4. SEM- photo of (a) the sintered coating surface with different magnifications, (b) the cross section (Thickness of the unsintered coating: 10 µm, $\Delta\vartheta\uparrow$ = 3.0 Ks^{-1}, ϑ_s = 1,450°C, t = 400 s, $\Delta\vartheta\downarrow$ = 0.38 Ks^{-1}, shielding gas)

within the ceramic and the boundary between metal and the ceramic can be minimised. Furthermore, compound formation will be favoured in the area of the highest temperatures.

2. In general, the two obviously different thermal expansion coefficients of both materials are assumed to be responsible for thermally-induced stresses and crack formation. However, in the cool down cycle, shrinkage of the metal, which has the higher expansion coefficient, can partially compensate for the reduction of the sintered volume of alumina.

To eliminate the previously mentioned influence of different thermal expansion coefficients, a new type of

steel with nearly the same thermal expansion coefficient as the ceramic material was chosen. Furthermore, only the Nd:YAG- laser was used for heating.

Sintering on steel 1.3981 by Nd: YAG- laser beam

Development of dense and crack-free coatings was made possible by the new material combination and the use of a Nd:YAG- laser.

A small window of parameters could be found, that leads to the best results ever achieved. Sintering temperatures just below the metal's melting point allow the generation of the intended coating properties within a minimal time-determined to be about 400 s sintering time. Higher temperatures or longer elapsed times result in the melting of the underlying metal substrate. Lower temperatures require a longer arrest time in the manner described below:

For a temperature of ϑ_s = 1,350°C, it will take about t = 700 s to sinter the coating.

For a temperature of ϑ_s = 1,300°C the time for the sintering process increases to t > 2000 s.

The resulting coatings are characterised by:

– A very fine-grained structure
– High density
– High adherence
– No cracks at equal layer thickness.

The grain size can be regulated as a function of the technological parameters. A minimum grain size leading to a dense sintered coating was determined to be 250 nm (the original grain size was 200 nm). The porosity determined was less than 6%. Figure 4(b) shows the cross section of the transition layer between the coating and metal. It is possible to see a gradient of density that grows with increased distance from the metal. The resulting hardness, determined by the Fraunhofer IKTS and confirmed by TU Chemnitz, is up to 20 GPa. This means that the hardness of the coatings is nearly the same as that of the compact alumina.

Conclusions

Laser sintering of alumina coatings on metals, without any liquid phase, have been studied for the first time.

It could be shown that the material combination, as well as the laser wavelength used, siginificantly influences the coating's quality. A material combination of nearly equal thermal expansion coefficients allowed the generation of crack-free laser sintered alumina by use of a Nd:YAG- laser beam. The coatings were characterised by a fine and controllable grain size, high hardness and adherence. In comparison with the alternative method -sintering in a furnace-, the main advantage is an achievable crack-free layer and very short processing times. It takes only 7 minutes to sinter with the laser beam, whereas the procedure in a furnace takes about five hours.

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